existence of the η- and θ-isomers[4] were not known at the time of these experiments, these and possibly other isomers may have been formed in small amounts. Also, secondary isomerization of primary products undoubtedly affected the final composition both qualitatively and quantitatively; the β-isomer in particular if formed should have largely isomerized to alpha. In view of these considerations the agreement of the observed results with those predicted appears sufficiently good to support the described mechanism. The ϵ-, η- and θ-isomers have not been available to us for isomerization so that we have not been able to use them to test the suggested mechanism.

We gratefully acknowledge the aid of Messrs. W. R. Harp, Jr., and F. S. Mortimer in making the spectroscopic analyses, and the suggestions of Dr. A. G. Kridl on the mechanism of isomerization.

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[4] A. J. Kolka, H. D. Orloff and M. E. Griffing, Abstracts of Papers, 121st Meeting of American Chemical Society, Buffalo, N. Y., March 24-27, 1952.

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Tracer-diffusion in Liquids. IV. Self-diffusion of Calcium Ion and Chloride Ion in Aqueous Calcium Chloride Solutions[1]

BY JUI H. WANG

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The salt diffusion of calcium chloride in its aqueous solutions has been the subject of experimental study of many workers in the past fifteen years. The results obtained by Harned and Levy[2] indicate that the measured salt diffusion coefficients of calcium chloride are lower than the values computed from the Onsager–Fuoss theory in solutions of concentration between 0.001 and 0.005 formula weight per liter. The salt diffusion coefficients of calcium chloride in concentrated aqueous solutions have been determined by Hollingshead and Gordon[3] and by Robinson and Chia[4] by means of the diaphragm cell method, and independently by Stokes and coworkers[5] and by Lyons and Riley[6] by means of the optical method. Their results show that in calcium chloride solutions of concentration above 0.2 formular weight per liter the salt diffusion coefficient increases with increasing salt concentration up to about 2.2 formular weight per liter. This phenomenon has generally been attributed to the continual decrease of the activity coefficient of the salt along the diffusion path. In self-diffusion, however, the chemical composition and hence the activity coefficient of the diffusing ions is constant along the diffusion path, the theoretical relationship between the diffusion coefficient and salt concentration becomes simpler and we may expect the shape of the D *vs.* $\sqrt{c}$ curves for self diffusion to be quite different from that for salt diffusion. Furthermore, it should be of interest to see how the self diffusion coefficients for different ions in the same solution vary as the salt concentration of the solution increases continually up to saturation. In the present work the self-diffusion coefficients of calcium ion and chloride ion in aqueous calcium chloride solutions at 25° have been measured by means of the improved capillary method.

Experimental

Radioactive Tracers.—Ca^{45} and Cl^{36} were used as tracers in the self-diffusion measurements. These were obtained from the Isotopes Division of the U. S. Atomic Energy Commission at Oak Ridge, Tennessee.

Diffusion Measurement.—The experimental techniques involved were already discussed in paper I of this series. The radioactivity of the diffusion samples was measured with a windowless, continuous flow counter. Since dry calcium chloride is hygroscopic in air, the calculated amount of sodium fluoride solution was added to each sample before evaporation to dryness under an infrared lamp. The samples so prepared contained approximately equal amounts of dry residue (solid sodium chloride and calcium fluoride) and were kept in a desiccator overnight before counting. Since in the calculations to obtain the diffusion coefficients only the ratio of the concentrations of radioactive tracers is involved, possible errors due to self-absorption of β-radiation are automatically eliminated.

Results.—The measured self-diffusion coefficients of Ca^{++} and Cl^- in aqueous calcium chloride solutions at 25° are listed in Table I. Each value listed in Table I is the average result of at least four measurements.

TABLE I

SELF-DIFFUSION COEFFICIENTS OF Ca^{++} AND Cl^- IN $CaCl_2$ (aq.) AT 25°

Concentration formular wt./liter	$D_{Ca^{++}} \times 10^5$, cm.²/sec.	$D_{Cl^-} \times 10^5$, cm.²/sec.
0.0100	0.778 ± 0.028	
.0705	.782 ± .015	1.89 ± 0.02
.282	.767 ± .008	1.72 ± .04
.803	.646 ± .025	1.60 ± .04
1.41	.560 ± .020	1.42 ± .03
2.68	.405 ± .015	0.907 ± .020
4.02	.225 ± .002	0.447 ± .015
5.36	.100 ± .009	0.159 ± .010

Discussion.—Using apropriate units the Onsager equation may be written as[7]

$$D_j = \frac{RT\lambda_j{}^0}{|Z_j|\mathfrak{F}^2}\,\frac{\lambda_j^0|Z_j|\mathfrak{F}}{3N\mathfrak{D}} \times 2.694 \times 10^{16} \times \sqrt{\frac{4\pi}{\mathfrak{D}RT}}\,[1 - \mathrm{d}(\omega_j)]\sqrt{\sum_i c_i Z_i{}^2} \quad (1)$$

where D_j is the tracer-diffusion coefficient of ions of the jth kind in a salt solution, Z_i is the charge in electronic units and c_i the concentration in moles per liter of ion i, $\lambda_j{}^0$ the limiting equivalent conductance of ion j, $\mathfrak{D}$ the dielectric constant of the solvent k the Boltzmann constant, $\mathfrak{F}$ the Faraday constant, T the absolute temperature, and $\mathrm{d}(\omega_j)$ a function given by

$$\mathrm{d}(\omega_j) = \frac{1}{\sum\limits_i c_i Z_i{}^2}\,\Sigma\,\frac{c_i|Z_i|\lambda_i{}^0}{(\lambda_i{}^0/|Z_i|) + (\lambda_j{}^0/|Z_j|)} \quad (2)$$

For the diffusion of tracer amount of ions of species 1 in salt solution containing ions of species 2 and 3, we have

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[1] Contribution No. 1134 from the Department of Chemistry of Yale University: Paper I, THIS JOURNAL, **74**, 1182, 6317 (1952); paper II, **74**, 1611 (1952); paper III, **74**, 1612 (1952).

[2] H. S. Harned and A. L. Levy, *ibid.*, **71**, 2781 (1949).

[3] E. A. Hollingshead and A. R. Gordon, *J. Chem. Phys.*, **9**, 152 (1941).

[4] R. A. Robinson and C. L. Chia, THIS JOURNAL, **74**, 2776 (1952).

[5] Hall, Wishaw and Stokes, private communication.

[6] P. A. Lyons and J. F. Riley, private communication.

[7] See paper I or II of this series.

$$c_1 \cong 0$$
$$c_2 |Z_2| = c_3 |Z_3|$$

and hence (2) can be written as

$$d(\omega_1) = \frac{|Z_1|}{|Z_2| + |Z_3|} \left[\frac{|Z_2| \lambda_2^0}{|Z_2|\lambda_1^0 + |Z_1|\lambda_2^0} \right] + \frac{Z_3 |\lambda_3^0}{|Z_3| \lambda_1^0 + |Z_1|\lambda_3^0} \Bigg] \tag{3}$$

If we take $\lambda^0_{\text{Cl}^-} = 76.36$, $\lambda^0_{\text{Ca}^{++}} = 59.4$, and using the relationship $\sum_i c_i Z_i^2 = 6c$ where c is the salt concentration in formular weight of $CaCl_2$ per liter of solution, we obtain by combining (1) and (3)

$$D_{\text{Ca}^{++}} \times 10^5 = 0.791 - 0.808 \sqrt{c} \tag{4}$$

and

$$D_{\text{Cl}^-} \times 10^5 = 2.033 - 1.729 \sqrt{c} \tag{5}$$

for the self-diffusion of Ca^{++} and Cl^-, respectively, in dilute calcium chloride solutions.

Values of $D_{\text{Ca}^{++}} \times 10^5$ and $D_{\text{Cl}^-} \times 10^5$ are plotted *vs.* $\sqrt{c}$ in Fig. 1. The two straight lines in the dilute concentration range represent equations (4) and (5), respectively.

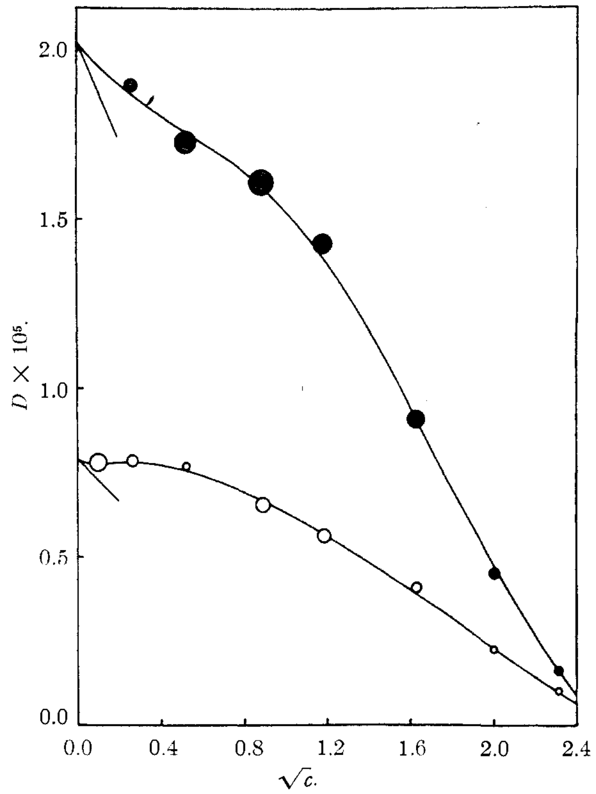

Fig. 1.—Self-diffusion coefficient of Ca^{++} and Cl^- in $CaCl_2$(aq.) at 25°: ●, self-diffusion of Cl^-; ○, self-diffusion of Ca^{++}.

It can be noticed from Fig. 1 that as the concentration of calcium chloride solution decreases continuously to zero the self-diffusion coefficients of both Ca^{++} and Cl^- appear to approach the Nernst's limiting values from above the two straight lines representing Onsager's equations (4) and (5). This tendency of approaching the limiting value from above Onsager's equation appears to be especially apparent in the self-diffusion of calcium ion. It is interesting to recall that an analogous behavior exists in the transference number data of calcium ion in dilute aqueous calcium chloride solutions.[8]

The general shapes of the curves in Fig. 1 are in apparent agreement with the general qualitative interpretation suggested in the three preceding papers of this series.[1] Thus because of the larger mean radius of the hydrated calcium ion and the fact that calcium chloride is a 2–1 electrolyte, all the previously mentioned "distortion-effect" on the structure of solvent water, "effect of sharing of hydration," etc., should become important at lower formular concentration of the salt for calcium chloride than for sodium or potassium chloride solutions.

It may also be noticed from the values listed in Table I that the ratio of the self-diffusion coefficient at infinite dilution to that in 5.36 formular wt. per liter calcium chloride solution is approximately 13 for Cl^- and 8 for Ca^{++}. The ratio of viscosity of 5.36 formular wt. per liter calcium chloride solution to that of pure water at 25° is about 11.

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[8] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 164.

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Local Anesthetics. III. Modifications of β'-4-Methylphenoxyethyl β-N-Methylbenzylaminoethyl Ether

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In papers I and II we have reported that the salts of aryl alkamine ethers $ArOR'NR_2$[1a] and aryloxyalkyl alkamine ethers $ArOR'OR''NR_2$[1b] in which Ar is an aryl, R' and R'' are alkylene and R is an alkyl or aralkyl group, have been tested as local anesthetics. As a continuation of this work, we have now prepared a number of compounds related to β-4-methylphenoxyethyl β'-N-methylbenzylaminoethyl ether which was reported in paper II[1b] to produce good corneal anesthesia.

Table I lists the compounds synthesized, with pertinent physical and analytical data. 'Solutions of hydrochlorides or other salts of these ethers were tested for local anesthetic activity by Dr. R. K. Richards and his staff to whom we are indebted. All these ethers displayed corneal and wheal anesthesia but the activity was accompanied by some irritation.

Experimental

The *o*-diphenoxyethoxyethyl chloride was prepared in 47.5% yield by a method Bruson[2] developed for analogous compounds. The boiling point of an analytical sample was 162° (1.0 mm.), n^{26}_D 1.5792.

Anal. Calcd. for $C_{16}H_{27}ClO_2$: C, 69.43; H, 6.19; Cl, 12.81. Found: C, 69.51; H, 6.29; Cl, 12.81.

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[1] (a) H. B. Wright and M. B. Moore, THIS JOURNAL, **73**, 2281 (1951); (b) **73**, 5525 (1951).

[2] H. A. Bruson, U. S. Patent 2,115,250, April 26, 1938.